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NRL Memorandum Report 5660

Electrochemical Properties of Palladium and Platinum Phosphine Complexes

J. M. CALVERT, B. H. BERRIE, R. J. NOWAK AND J. C. COOPER

Surface Chemistry Branch
Chemistry Division

September 30, 1985

NAVAL RESEARCH LABORATORY
Washington, D.C.

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REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION	1b RESTRICTIVE MARKINGS
UNCLASSIFIED	
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited.
4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S)
NRL Memorandum Report 5660	

6a NAME OF PERFORMING ORGANIZATION	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION
Naval Research Laboratory	Code 6173	

6c ADDRESS (City, State, and ZIP Code)	7b ADDRESS (City, State, and ZIP Code)
Washington, DC 20375-5000	

8a NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
	(See page ii)			

11 TITLE (Include Security Classification)

Electrochemical Properties of Palladium and Platinum Phosphine Complexes

12 PERSONAL AUTHOR(S)
Calvert, J.M., Berrie, B.H., Nowak, R.J. and Cooper, J.C.

13a TYPE OF REPORT	13b TIME COVERED		14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Interim	FROM ___	TO ___	1985 September 30	37

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Palladium phosphine complexes Carbon dioxide reduction
			Electrochemistry

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The electrochemistry of 11 palladium (II) and platinum (II) complexes of the type ML_2X_2 (L = P, N, or C-donor; X = Cl or I) was examined by cyclic voltammetry in nonaqueous solution. Electrochemical reduction was irreversible and was coupled with loss of X^-. Equilibria between the metal complexes and added L significantly altered the observed electrochemistry.

Reduction peak potentials for a homologous series of complexes qualitatively reflected expected ligand field strengths. Agreement was also found between the optical d-d transition energy and the electrochemical reduction potential for selected complexes. *Trans-* isomers were harder to reduce than *cis-* isomers by about 300 mV. A shift of approximately 400 mV to more negative potentials was determined for the reduction of Pt(II) relative to Pd(II) for complexes with identical coordination environments.

Saturation of the solution with carbon dioxide had no effect on the cyclic voltammetric behavior of the complexes.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION	
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	UNCLASSIFIED	
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL
J. C. Cooper	(202) 767-3115	Code 6173

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted
All other editions are obsolete

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61153N			61-1746-A-5
62543N			61-1866-0-5

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QUALITY
INSPECTED

A-1

iii

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ELECTROCHEMICAL PROPERTIES OF PALLADIUM AND PLATINUM PHOSPHINE COMPLEXES

INTRODUCTION

The thermodynamic values for the reduction of carbon dioxide in aqueous solution are given below [1]:

$$E^O \text{ (V vs. NHE)}$$

$CO_2 + 2H^+ + 2e^- \longrightarrow HCOO^-$ or $HCOOH$	-0.20 (1)
$2CO_2 + 2H^+ + 2e^- \longrightarrow C_2O_4^=$ or $H_2C_2O_4$	-0.49 (2)
$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$	-0.1 (3)
$CO_2 + 4H^+ + 4e^- \longrightarrow C + 2H_2O$	$+0.21$ (4)
$CO_2 + H_2O + 2e^- \longrightarrow HCOO^- + OH^-$	-0.72 (5)
$2H^+ + 2e^- \longrightarrow H_2$	0.00 (6)
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	-0.83 (7)

The results of previous voltammetric studies have shown that reduction of CO_2 in aqueous solution occurs as an irreversible process at a mercury cathode at $E^{O\prime} = -2.40V$ vs. NHE and proceeds according to reaction (1) above, i.e., formic acid or formate is the exclusive product of electrolysis [2]. The reasons for this are:

(a)   Protonation of reduced CO_2 is faster in water than coupling to give oxalate (reaction 2).

(b)   Structural and mechanistic demands of reactions 3 and 4 impose large overpotentials in addition to the thermodynamic potential, rendering these pathways less favorable than reaction 1.

(c)   Hg electrodes possess a high overpotential for the evolution of hydrogen, and therefore cause reaction 6 and 7 to be more difficult than reaction 1. Similar results have been observed with lead, indium, cadmium, tin, zinc, gold and carbon cathodes [3,4].

The low electrochemical activity of CO_2, as evidenced by the extreme potentials necessary to achieve its reduction, has prevented the electrolysis cells constructed to date from achieving suitably high conversion efficiencies and turnover rates.

This report describes the electrochemistry of a family of monomeric and dimeric palladium and platinum phosphine complexes that are potential CO_2 reduction catalysts.

The catalytic properties of phosphine complexes of the platinum group metals are well known [5]; however, only recently has attention been turned to them for use in the transformation of CO_2 into other C_1 (or higher) chemical feedstocks such as formic acid, methanol and oxalic acid [6].

One important pathway that has been elucidated for the transition metal catalyzed reduction of carbon dioxide is reaction of CO_2 with a metal-hydride bond [7]. The insertion of

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CO_2 into a metal-hydride bond in non-aqueous solution is well-known: The reversible insertion of CO_2 into a platinum phosphine dihydride to form a monodentate formate complex [8] is shown in Equation (8). This reaction also occurs with low-valent

$$Pt(PEt_3)_3H_2 + CO_2 \iff Pt(PEt_3)_3H(O-C=OH) \qquad (8)$$
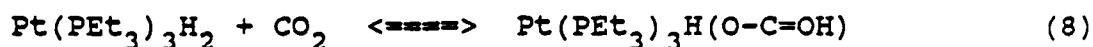
complexes of Rh [9], Fe [10], Co[11], Ru[12], Cr[13], Mo[13], and W[13]. The reverse of the insertion reaction -- metal hydride formation via loss of CO_2 -- has also been observed (Equation (8)).

$$[M(CO)_5(O-C=OH)]^- \iff [HM(CO)_5]^- + CO_2 \qquad (9)$$
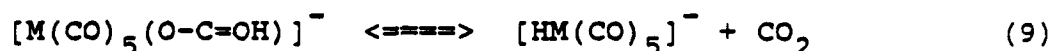
Thus, a simplistic catalytic cycle can be drawn as shown in Figure 1 which involves metal-hydride and metal-COOH (where the binding site, C or O, is not specified) intermediates. The net reaction (Equation 10) is the reduction of CO_2 with H_2 to formic acid.

$$CO_2 + H_2 \longrightarrow HCOOH \qquad (10)$$

Another criterion for successful catalysts is that there be available multiple stable oxidation states, since the chemical transformations of the substrate are typically multi-electron processes (see Equations 1 - 7). Low-valent states, in particular, must be accessible. The existence of dimeric complexes is of great potential utility in that multi-electron processes may be effected more easily because of the contributions from two metal centers.

Taking all of these considerations into account, palladium phosphine complexes merited investigation. Some background synthetic chemistry exists; Pd-hydrides and dimers are known. Metal oxidation states 0, I, II and IV are available.

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To assess the potential utility of these complexes as CO_2 reduction catalysts, their redox characteristics were studied using electrochemical techniques. This part of the report details the results obtained with a series of palladium phosphine monomers and dimers.

EXPERIMENTAL

The metal complexes were either synthesized as described previously [14] or were purchased from Alfa. Additional phosphines used in the electrochemical experiments were reagent grade. Electronic absorption spectra were obtained with a Cary 14 spectrophotometer.

Electrochemistry was performed using conventional instrumentation. Electrolyte solutions were either 0.1M tetra-$\underline{n}$-butyl-ammonium perchlorate (TBAP) in acetonitrile (AN), or 0.2M TBAP in methylene chloride (MC). Solvents (Burdick & Jackson) were stored over activated Davisson 3Å molecular sieves for at least 24 hours before use. Electrolytes (Southwestern Analytical) were dried in a vacuum oven for 12 h. at 60°C and stored in a desiccator. Inert gas was solvent-saturated before introduction to the cell. Electrodes employed were Pt microdisk (working) and Pt coil (auxiliary). All potentials are referenced to the saturated sodium chloride calomel electrode (SSCE). The concentration of complex was typically about 10^{-4}M ; these were saturated solutions due to low solubility. The tri($\underline{n}$-butyl)phosphine complexes were an exception; their greater solubility allowed concentrations in the millimolar range.

RESULTS AND DISCUSSION

The electrochemistry of the following complexes was investigated by cyclic voltammetry: $\underline{trans}$-Pd^{II}L$_2$X$_2$, where L = PPh$_3$, PBu$_3$, PCy$_3$, NHMe$_2$ (Ph = phenyl, Bu = $\underline{n}$-butyl, Cy = cyclohexyl, Me = methyl) and X = Cl or I; $\underline{cis}$-Pd^{II}(LL)X$_2$, where LL = 2,2'-

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bipyridine (bpy), 1,5-cyclooctadiene (COD), diphenylphosphino-
methane (dppm) and 1,2-diphenylphosphinoethane (diphos);
$M^I_2(\mu\text{-dppm})_2Cl_2$ (M = Pd, Pt); cis-$Pt^{II}(PPh_3)_2Cl_2$.

1. trans-PdL_2X_2 and cis-$Pt(PPh_3)_2Cl_2$

A) Electronic Spectra. The UV-Vis spectra of trans-
$Pd(PR_3)_3Cl_2$ (R = Bu, Cy and Ph) in CH_3CN solution are shown in
Figure 2. The spectra were invariant over a period of several
hours, indicating that the Pd(II) complexes were stable in
solution. A single structureless absorption band was observed,
the peak positions of which are listed below.

$Pd(PBu_3)_2Cl_2$	323 nm
$Pd(PCy_3)_2Cl_2$	344 nm
$Pd(PPh_3)_2Cl_2$	345 nm

The peaks are assigned to ligand field transitions based on
detailed spectroscopic investigations of the analogous platinum
complexes by Geoffroy [15]. A molecular orbital energy diagram
for square planar phosphine complexes from that report is repro-
duced in Figure 3. Modification of the diagram to reflect the
presence of the weaker-field halide ligands would include
lowering the energy of the highest empty metal-based orbital (d_{xy}
or $d_{x^2-y^2}$, depending on symmetry) to below the phosphine π^*
orbital, and inclusion of chloride π orbitals below the filled d
orbitals.

The ordering of the transition energies: R = Bu > Cy, Ph is
a reflection of the ligand-field splitting, Δ , in the MO diagram

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and gives an indication of the relative ligand-field strength of the various phosphines. The implication of this information is that electrochemical reduction of these complexes will involve placing an electron(s) in an empty metal-based orbital, and the same energy ordering should be maintained in the electrochemical reduction potentials.

B) Electrochemical Properties. Electrochemical data are summarized in Table 1.

The cyclic voltammogram (CV) of trans-Pd(PBu$_3$)$_2$Cl$_2$ in TBAP/AN electrolyte ([complex] = 2 mM) is shown in Figure 4. The complex exhibits a completely irreversible reduction at $E_{p,c}$ = -1.78 V. No return wave can be detected at sweep rates of up to 500 mV/s. The peak potential varies somewhat with sweep rate. An irreversible anodic wave is present at $E_{p,a}$ = +1.68 V.

By analogy to the reported CV behavior of the related Pt-PPh$_3$ complex [16] (also investigated here), these processes most likely correspond to a metal-centered, two-electron reduction and oxidation (Equations 11 and 12, respectively). There is evidence

$$Pd(II) + 2e^- ----> Pd(0) \qquad (11)$$
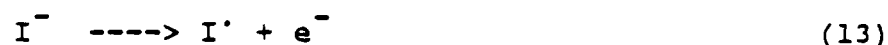
$$Pd(II) ----> Pd(IV) + 2e^- \qquad (12)$$
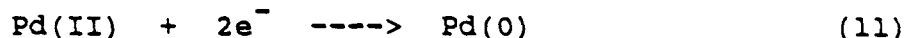
in the CV for the ejection of chloride ion from the Pd(0), as was claimed for Pt (although not demonstrated in the voltammetry) [16,17]. While it is possible that the reduced complex remains intact, it is unlikely in view of the greater lability of second-row transition metals in relation to third-row metals.

The electrochemistry of trans-Pd(PBu$_3$)$_2$I$_2$ was also investigated. CV of the iodo complex (Figure 5) using a 200 mV/s sweep

rate gave an irreversible, presumably $2e^-$, reduction at $E_{p,c} =$ -1.61 V. The shift of the peak potential to a less negative value (about 85 mV per iodide) is reasonable because I^- is a weaker ligand than Cl^-, which results in a reduced ligand field splitting and a lowering of the energy of the $d\pi^*$ orbital.

Two well-defined anodic peaks were present at $E_{p,a} = +0.33$ and +0.63 V only after generation of a Pd(0) complex. These waves are attributable to the presence of free I^- which is liberated from the reduced complex. The size of the peaks is significantly smaller than would be expected for a one-electron process, i.e.,

$$I^- \longrightarrow I^{\cdot} + e^- \tag{13}$$

$$2I^{\cdot} \longrightarrow I_2 \tag{14}$$

$$I_2 + I^- \longrightarrow I_3^- \tag{15}$$

$$I_3^- \longrightarrow I_3^{\cdot} + e^- \tag{16}$$

It can then be inferred that there is an equilibrium between the reduced PdL_2I_2 complex (or other iodide-containing product) and the resultant dissociated species and free I^- that favors the undissociated form:
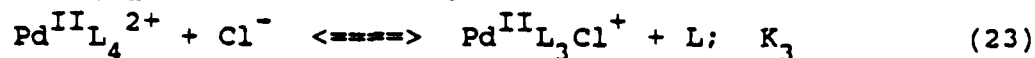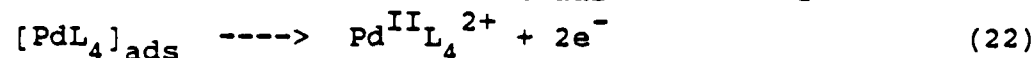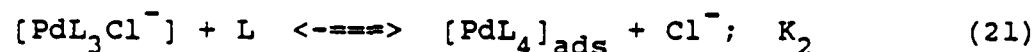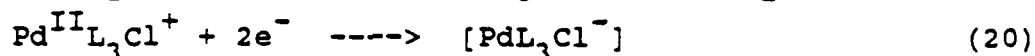
$$PdP_2I_2 + 2e^- \longrightarrow [PdP_2I_2]^{2-} \tag{17}$$

$$[PdP_2I_2]^{2-} \Longleftrightarrow [PdP_2I]^- + I^- \tag{18}$$
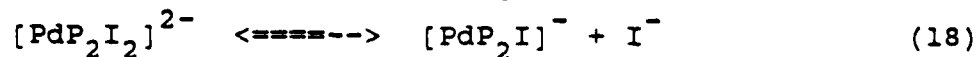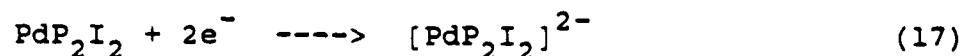
Since I^- is a weaker ligand and also a better leaving group than Cl^-, the inability to observe free chloride in the CV of PdP_2Cl_2 may be rationalized on the basis of an equilibrium similar to Equation 18 which lies even further to the left.

The CV of the chloro complex was also investigated with a three-fold excess of PBu_3 added to the electrolyte (Figure 6). An initial sweep to positive potentials (v = 100 mV/s) revealed the

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presence of two irreversible waves, which are likely attributable
to free Cl^- and PBu_3. The reductive sweep gave an irreversible
cathodic peak at $E_{p,a}$ = -1.18 V and a sharp, irreversible anodic
peak of approximately equal area at $E_{p,a}$ = -0.52 V. The anodic
peak is only present if the reductive peak has been traversed.

The observed behavior can be explained by the following
sequence: replacement in bulk solution of Cl^- by PBu_3 to form
$Pd(PBu_3)_3Cl^+$; reduction of the tris-phosphine complex to Pd(0);
replacement of the last chloride to form neutral PdL_4 which is
adsorbed onto the electrode. The subsequent sharp anodic
"stripping" peak is caused by the desorption of the tetrakis-
(phosphine) complex, following oxidation to Pd(II). The latter
species may be in equilibrium with free Cl^-. The reaction
sequence described above is summarized in Equations 19 - 23.

$$Pd^{II}L_2X_2 + L \ \Longleftrightarrow \ Pd^{II}L_3X^+ + Cl^-; \ K_1 \qquad (19)$$

$$Pd^{II}L_3Cl^+ + 2e^- \ \longrightarrow \ [PdL_3Cl^-] \qquad (20)$$

$$[PdL_3Cl^-] + L \ \Longleftrightarrow \ [PdL_4]_{ads} + Cl^-; \ K_2 \qquad (21)$$

$$[PdL_4]_{ads} \ \longrightarrow \ Pd^{II}L_4^{2+} + 2e^- \qquad (22)$$

$$Pd^{II}L_4^{2+} + Cl^- \ \Longleftrightarrow \ Pd^{II}L_3Cl^+ + L; \ K_3 \qquad (23)$$
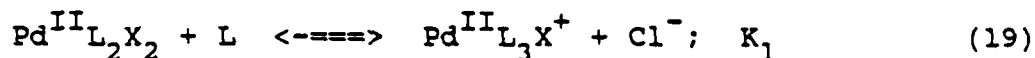
When the same experiment was conducted in the presence of
excess PPh_3 instead of PBu_3, the overall CV pattern was similar.
The major difference was that re-oxidation of the reduced species
gave three anodic peaks which range between -0.35 and -0.10 V.
These can be assigned to the oxidation of a variety of PdL_4
species which have different combinations of PBu_3 and PPh_3
ligands, suggesting that chloride ions are expelled from the
zerovalent Pd to reduce the charge on the complex and the surplus

of electron density at the metal center.

Several other observations can be made regarding the data in Table 3:

A) The tri(cyclohexyl) phosphine complex is reduced more easily than the tri(butyl) complex, although both are alkyl phosphines. This greater ease of reduction may be a result of the much bulkier nature of the PCy_3 ligand (11), producing a weaker interaction with the metal. The effect of the large cone angle of PCy_3 is also manifested in the experiment with added PCy_3. In this case the initial reduction is at -1.7 V, a potential characteristic of the PdP_2Cl_2 complex as opposed to a more highly phosphinated species. However, the Pd(0) form is sufficiently nucleophilic that partial formation of the PdP_4 complex is observed ($E_{p,a}$ = -0.05 V).

B) In the presence of added PPh_3, small peaks are present in the CV of $Pd(PPh_3)_2Cl_2$ which indicate the presence of tris- and tetrakis-phosphine species, in accord with the reaction sequence described above.

C) The CV of the dimethylamine complex could not be interpreted because the initial reductive sweep gave rise to hysteresis and the formation of a gray film on the electrode. The cause of this phenomenon is not understood, although the relatively mild potential argues against reduction of the amine ligand.

D) The electrochemistry of cis-$Pt(PPh_3)_2Cl_2$ was investigated for comparison with the palladium complexes, and to resolve confusion in the literature concerning its CV behavior [16,17].

The predicted two-electron irreversible reduction of Pt(II) was observed at -1.73 V, with no significant anodic counterpart being apparent. From the reported [17] difference between the cis- and trans- isomers of 240 mV ($E_{p,c}$ = -1.80 (trans), -1.56 (cis) vs. SSCE), the potential of the trans- Pt complex under the present conditions can be estimated as -1.97 V. Thus, the effect of changing the metal from Pd to Pt makes the complex more difficult to reduce by approximately 400 mV.

Addition of a small amount of free PPh_3 to the solution resulted in the appearance of a small peak at $E_{p,c}$ = -0.98 V, a concomitant decrease in the height of the -1.73 V peak, and the appearance of an anodic peak ($E_{p,a}$ = -0.08 V) of the same size as the new cathodic peak (Figure 7). Further additions of PPh_3 increased the height of the -0.98 V peak at the expense of .the more negative peak. This clearly demonstrates the existence of an equilibrium between the bis- and tris-phosphine M(II) complexes.

2. cis-Pd(II)(LL)X$_2$ Complexes

The electrochemistry of this group of complexes follows the same basic pattern as observed for the monodentate ligands, with some important differences due to the bifunctional nature of the ligand (LL). The data are summarized in Table 2.

The CV of cis-Pd(dppm)Cl$_2$ in TBAP/MC solution is shown in Figure 8. An initial sweep from 0.0 V to and from the oxidative limit reveals no electroactivity. Extending the sweep to negative potentials shows a well-defined, completely irreversible wave at $E_{p,c}$ = -1.29 V. The difference in potential between this complex and the trans Pd-PPh_3 complex compares favorably to the shift

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described previously for isomeric $Pt(PPh_3)_2Cl_2$ complexes (300 vs. 240 mV). Several small anodic peaks are produced as a result of the reduction. On the basis of the preceeding discussion, the cathodic peak can be assigned to the two-electron reduction of the dichloro complex. Free chloride ion is not detected.

Addition of free dppm to the solution caused an immediate deepening in color of the initially yellow solution. The CV of the mixture was much more complex, featuring two irreversible reductions at $E_{p,c}$ = -0.97 and -1.75 as well as two smaller, irreversible anodic peaks at -0.20 and +0.05V. The color change and the electrochemistry both suggest that the dppm has coordinated to Pd, however the CV characteristics do not fit the previously observed reaction patterns. Possible Pd-containing species which may be in solution include square-planar $Pd(dppm)_2{}^{2+}$, square-pyramidal $Pd(dppm)_2Cl^+$ and dimeric $Pd_2(\mu-dppm)_2Cl_4$. It was not possible to differentiate among these.

The electrochemistry of cis-Pd(diphos)Cl_2, which is only slightly soluble in the TBAP/MC electrolyte solution is shown in Figure 9. The CV reveals the expected irreversible reduction at $E_{p,c}$ = -1.28 V, a potential which is characteristic of the two-electron reduction of cis-phosphine complexes. The other feature of the voltammogram is a quasi-reversible couple ($i_{p,c} > i_{p,a}$) with $E^{\circ\prime}$ of about -0.6 V.

Addition of excess diphos to the solution causes the current corresponding to the couple to become much larger than that of the more negative peak (Figure 10). The resultant couple at $E^{\circ\prime}$ = -0.61 V is chemically reversible (equal peak currents). The

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observed behavior indicates that the species responsible for this couple is a product of the reaction of starting complex with diphos, possibly either $Pd(diphos)_2^{2+}$ or $Pd(diphos)_2Cl^+$. However, the number of electrons involved in the redox process cannot be determined from the observed peak splitting of 90 mV. Although closer to the value of 60 mV expected for a one-electron transfer as opposed to 30 mV for a two-electron event, kinetic restrictions (e.g., slow heterogeneous electron transfer, or structure reorganizational changes associated with a $2e^-$ change) could well produce this peak separation.

The electrochemistry of the other chelate complexes, $Pd(COD)Cl_2$ and $Pd(bpy)I_2$, was similar to that of the diphos complex in that the principal reductive process occured at a potential characteristic of a bis-chelate entity. A second similarity is that the definition of the voltammetry improves upon addition of excess chelate. The COD complex in the presence of excess COD gives an irreversible peak at -1.22 V ($2e^-$ reduction of $Pd(COD)Cl_2$) and two coupled irreversible peaks at $E_{p,c}$ = -0.7 and $E_{p,a}$ = +0.5 which are most likely due to the square planar or square pyramidal bis-COD complexes. Repeated cycling resulted in the formation of a gray film on the electrode surface.

For the bpy complex with added bpy, a wave for the dichloro species is not well-defined; the CV consists only of the coupled cathodic and anodic peaks at -0.6 V and +0.9 V, respectively.

3. $M^I_2(\mu-dppm)_2Cl_2$

The electrochemistry of the Pd and Pt dppm-bridged dimers

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was examined in TBAP/MC electrolyte, as shown in Figures 11 and 12. The CV of the Pd complex displays several cathodic peaks: a small wave at -0.35 V and a much larger, multi-component peak centered at -1.45 V. An anodic peak of intermediate size is present at +0.85 V; it is not a product of the reductive cycling. Addition of excess dppm causes the yellow solution to become orange, and the CV is dominated by a set of irreversible waves at $E_{p,c}$ = -1.00 V and $E_{p,a}$ = -0.26 V.

The Pt complex gives two small irreversible reductive peaks at $E_{p,c}$ = -0.95 and -1.18 and a much larger one at -1.40. A small anodic wave is also present at $E_{p,a}$ = -0.48 V. These narrow, but do not shift in the presence of excess phosphine -- perhaps reflecting slower substitution at Pt than Pd.

Depending on the extent of metal-metal interaction, a single net $2e^-$ reduction or two sequential $1e^-$ reductions would be expected for linked univalent metal centers. The appearance of a third cathodic peak may be due to the presence of Pd(II) impurities.

4. Electrochemical Reduction of Pd Complexes in a CO_2 Atmosphere.

It has been previously demonstrated that complexes which are produced by the $NaBH_4$ reduction of Pd(II)-phosphines react with carbon dioxide in homogeneous solution [18]. To compare the reactivity of the chemically and electrochemically generated forms, the voltammetry of three complexes -- $Pd(PBu_3)_2Cl_2$, $Pd(PBu_3)_2I_2$ and $Pd(PPh_3)_2Cl_2$ -- was examined in CO_2 and N_2-saturated CH_2Cl_2 solution. CV revealed no current enhancement (catalytic wave) at the Pd(II) --> Pd(0) wave, nor were any new

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product peaks observed.

The homogeneous experiment is known to give rise to a Pd^I metal-metal bonded dimer [18] which then reacts with CO_2. Binding is thought to occur by nucleophilic attack of the localized electron density in the Pd-Pd bond [14, 19] at carbon of CO_2. The explanation for the discrepancy between the chemical and electro-chemical results may be due to the fact that only a small quantity of reduced complex is produced in the electrochemical experiment, and that reaction with CO_2 is slow under these conditions.

TABLE 1. Electrochemical Properties of ML_2X_2 Complexes.

Complex	$E_{p,c}$ [a]	$E_{p,c}$; $E_{p,a}$ (xs L) [a]
$Pd(PBu_3)_2Cl_2$ [b]	-1.78	-1.18; -0.52;
		-1.15; -0.35,-0.23,-0.09 [c]
$Pd(PBu_3)_2I_2$	-1.61	-----
$Pd(PCy_3)_2Cl_2$	-1.63	-1.7; -0.03
$Pd(PPh_3)_2Cl_2$	(-1.6) [d]	-1.1; -0.1 [e]
$Pd(NHMe_2)_2Cl_2$	>-1.15 [f]	-----
$Pt(PPh_3)_2Cl_2$ [g]	-1.78	-0.98; -0.08

[a] All potentials are in volts vs. SSCE; sweep rate was 0.2 V/s.

[b] All Pd complexes are trans- isomers.

[c] Excess PPh_3 instead of PBu_3.

[d] Estimated from spectral data due to complex insolubility.

[e] Small poorly-defined peaks.

[f] Uncertain due to film formation.

[g] cis- isomer.

TABLE 2. Electrochemical Properties of <u>cis</u>-Pd(LL)X$_2$ Complexes

Complex	$E_{p,c}$[a]	$E_{p,c}$; $E_{p,a}$ (xs L)[a]
Pd(dppm)Cl$_2$	-1.30	-0.93, -1.73; -1.20, -0.23
Pd(dppm)I$_2$	-1.08	-----
Pd(diphos)Cl$_2$	-1.28	-0.65; -0.56
Pd(COD)Cl$_2$	-----	-0.48; +0.53
Pd(bpy)Cl$_2$	-----	-0.6; +0.9

[a] All potentials are in volts vs. SSCE

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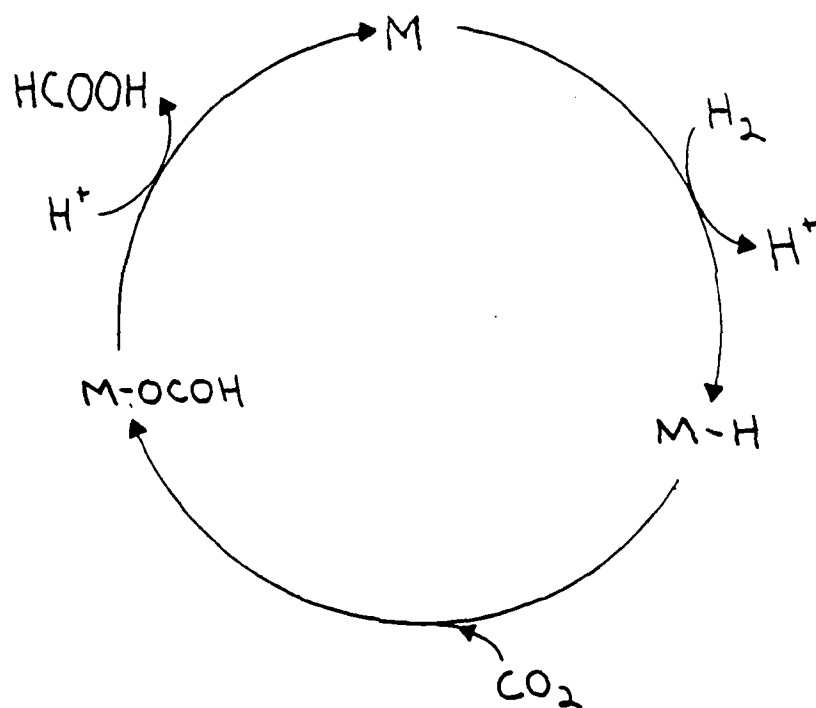
Figure 1. Example of a Catalytic Cycle for Carbon
Dioxide Reduction

trans- $Pd(PR_3)_2Cl_2$

$R = \underline{n}-Bu$

$R = Ph$

$\lambda \ (nm)$

Figure 2. UV-Vis Spectra of trans-$Pd(PR_3)_2Cl_2$
(R = Ph, Bu) in CH_3CN solution
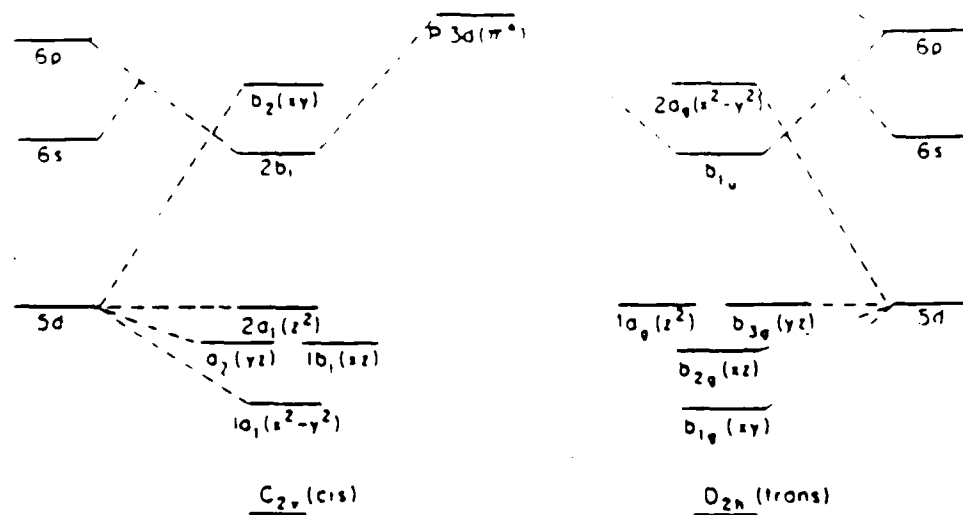
Figure 3. Molecular Orbital Energy Diagram for Square Planar Pd-Phosphine Complexes
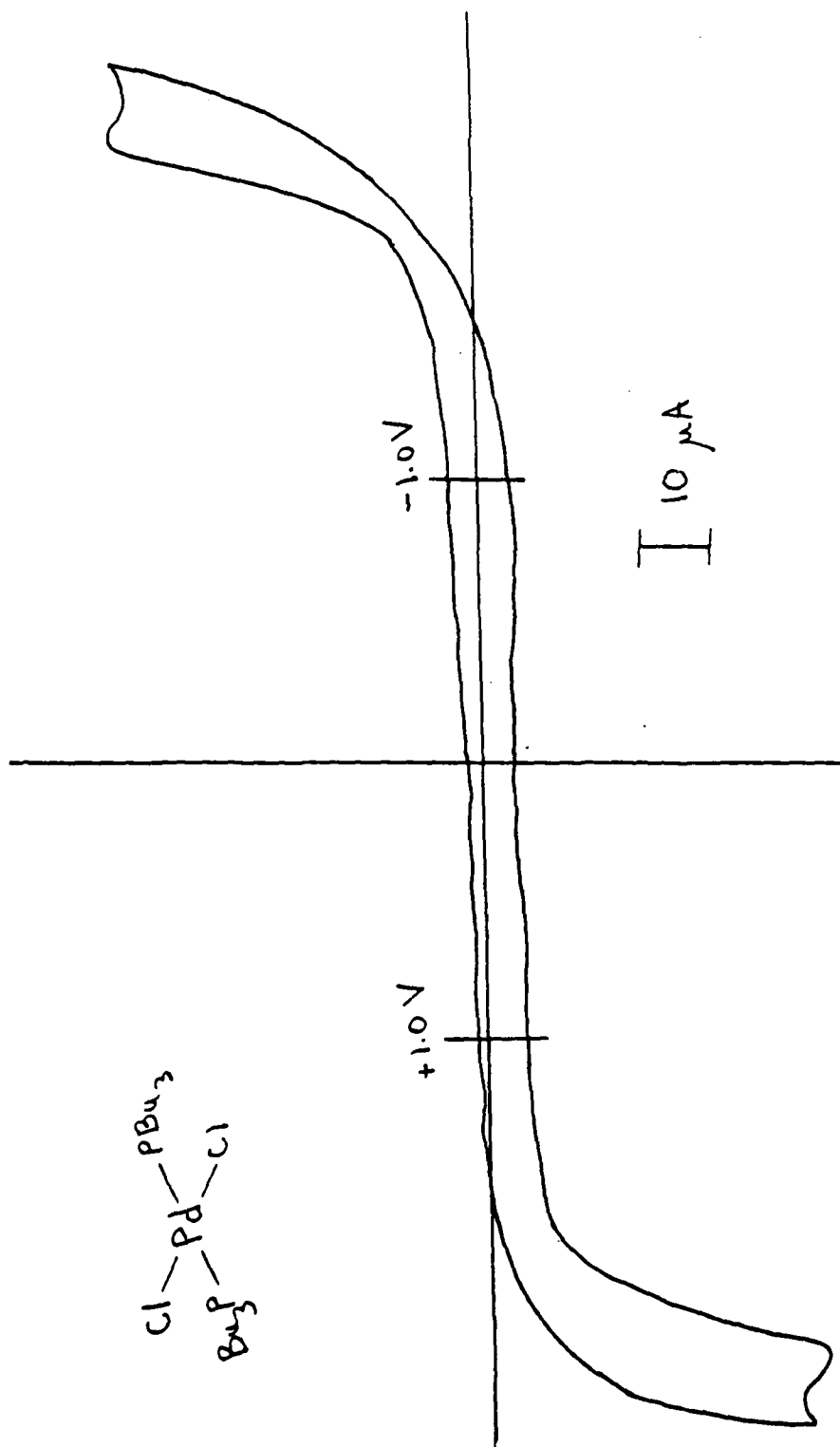
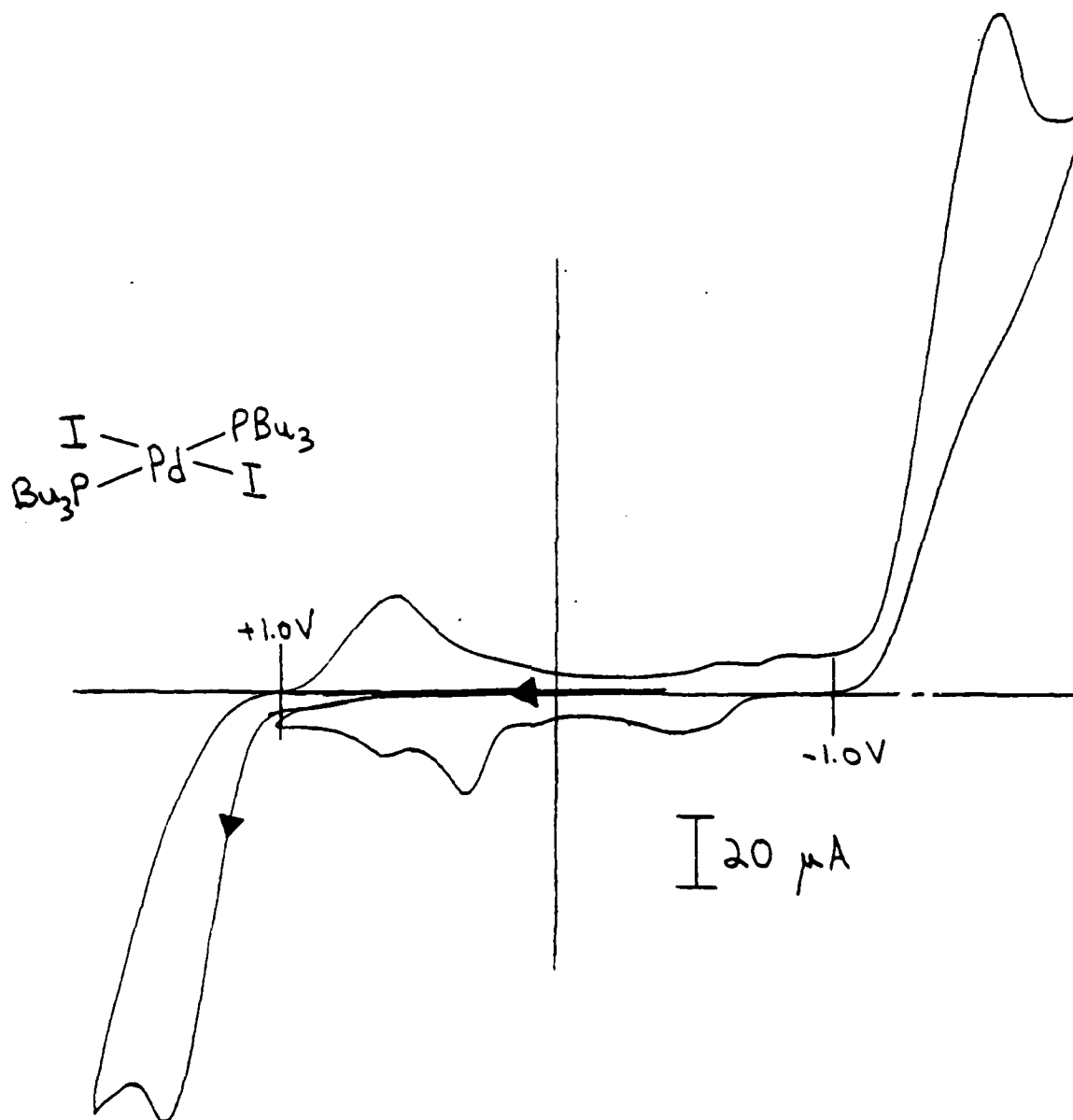Figure 4. Cyclic Voltammogram (CV) of trans-Pd(PBu$_3$)$_2$Cl$_2$ in TBAP/CH$_3$CN electrolyte

Figure 5. CV of _trans_-Pd(PBu$_3$)$_2$I$_2$ in TBAP/CH$_2$Cl$_2$
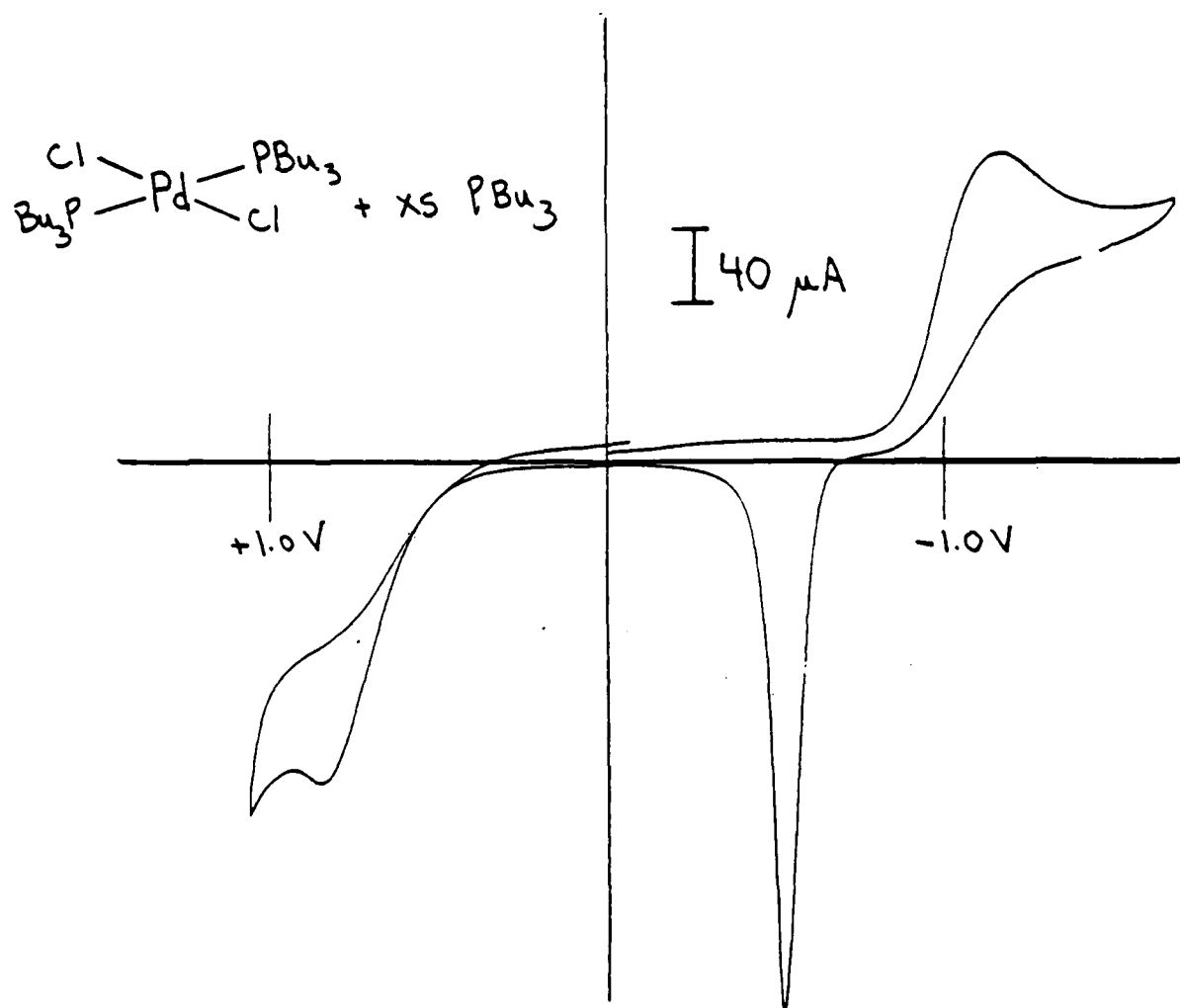
Figure 6. CV of <u>trans</u>-Pd(PBu$_3$)$_2$Cl$_2$ in TBAP/CH$_3$CN in the presence of a three-fold excess of PBu$_3$

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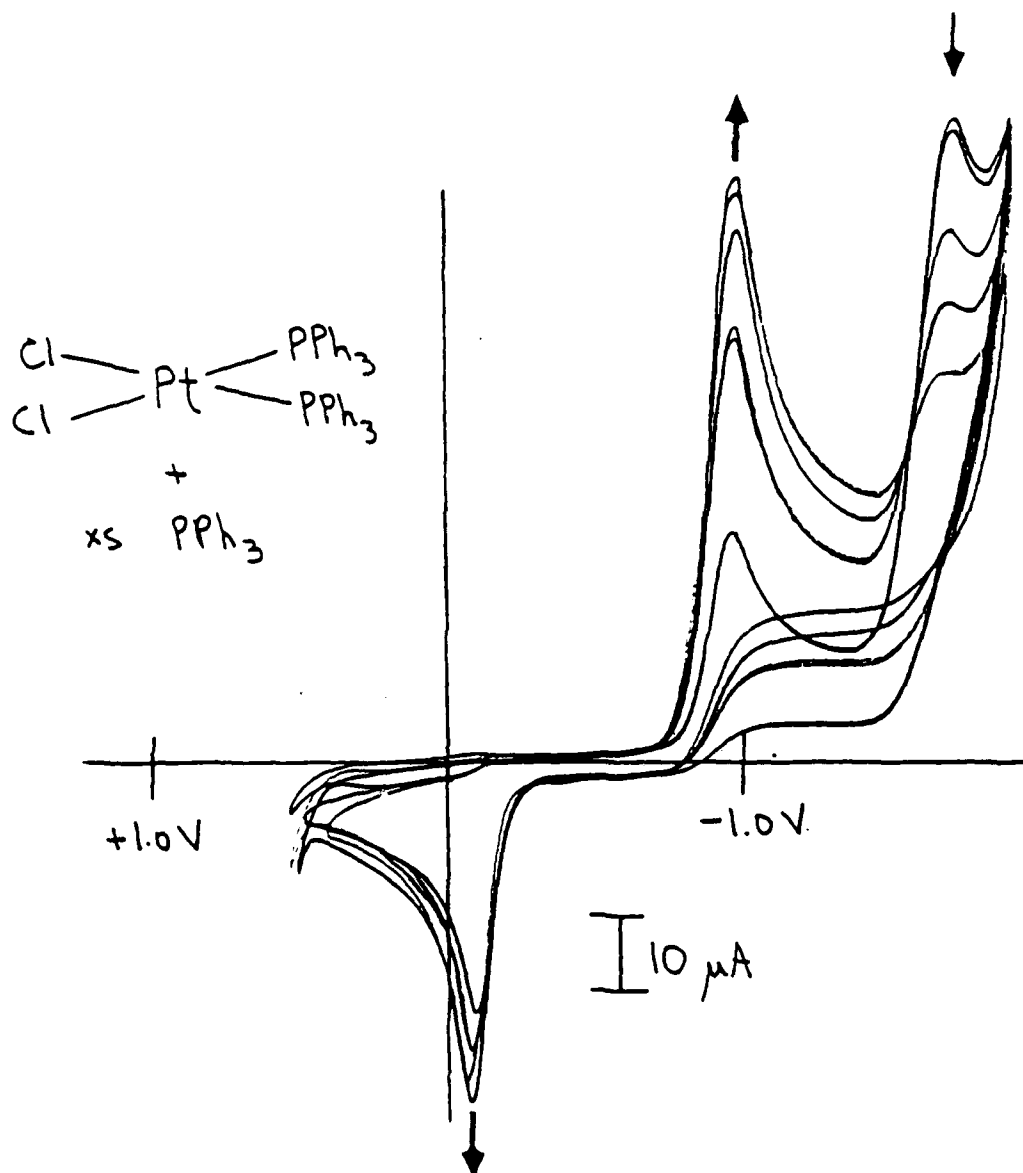
Figure 7. Sequential voltammograms of <u>cis</u>-Pt(PPh$_3$)$_2$Cl$_2$, recorded after repeated additions of free PPh$_3$
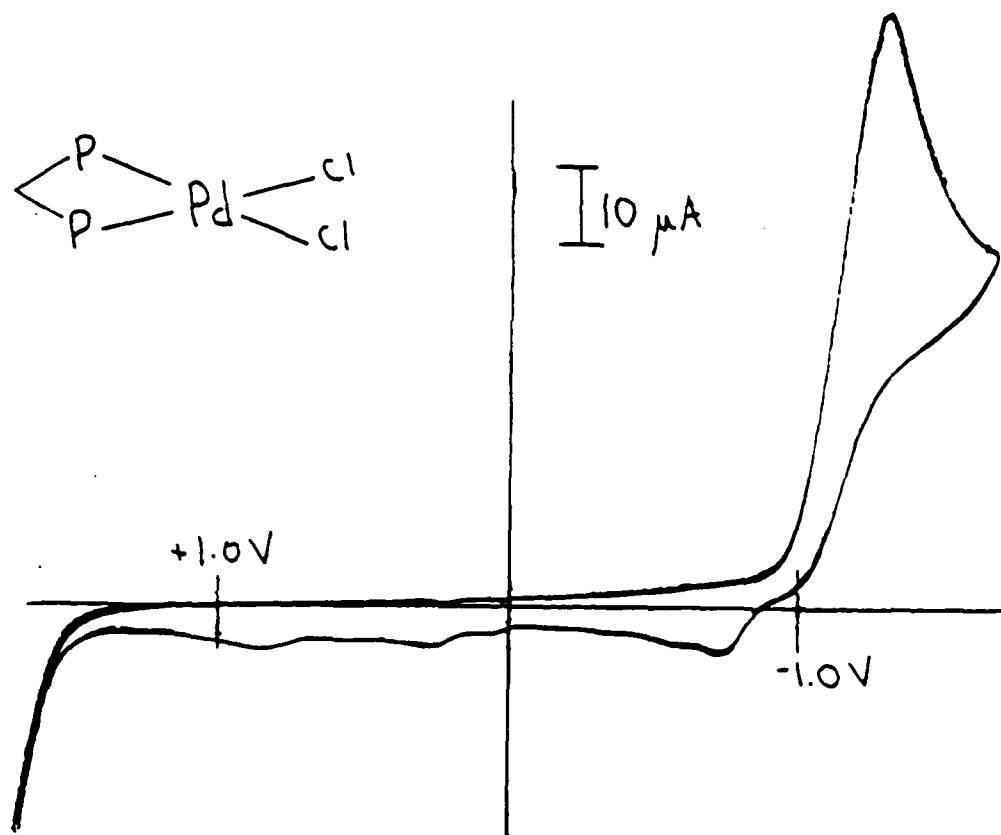
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Figure 8. CV of _cis_-Pd(dppm)Cl$_2$ in TBAP/CH$_2$Cl$_2$
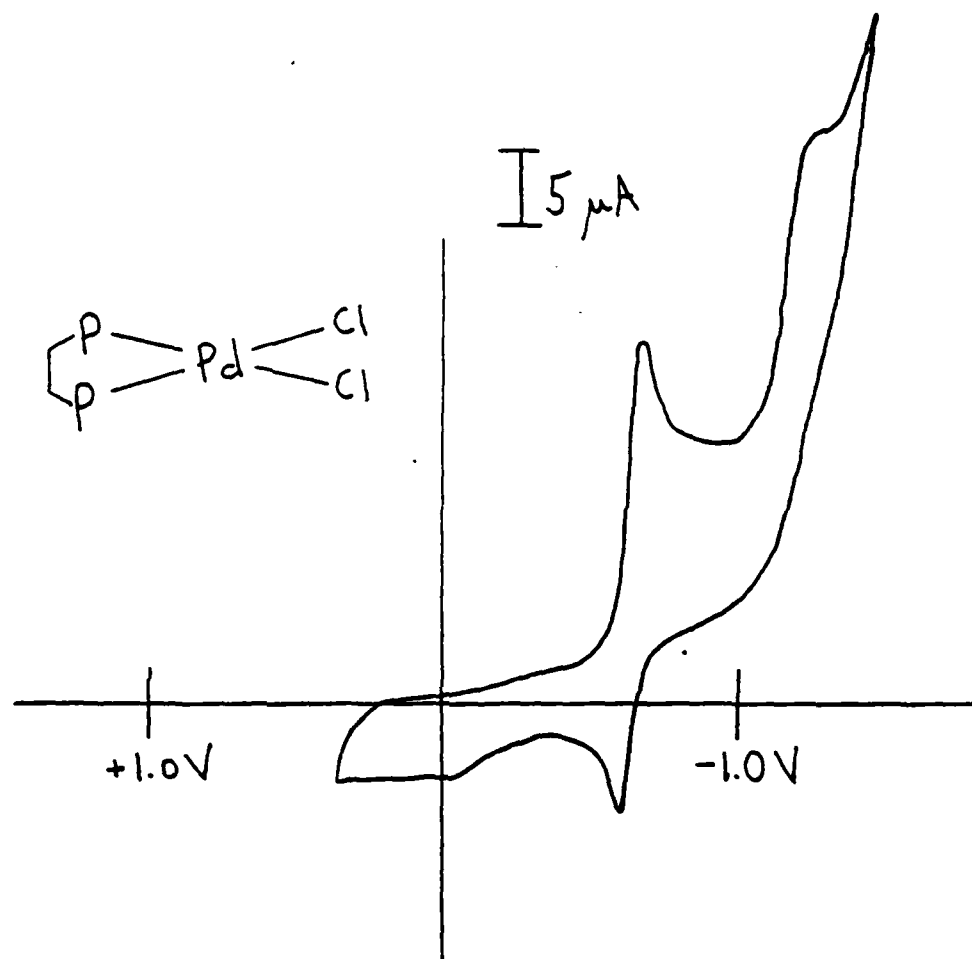
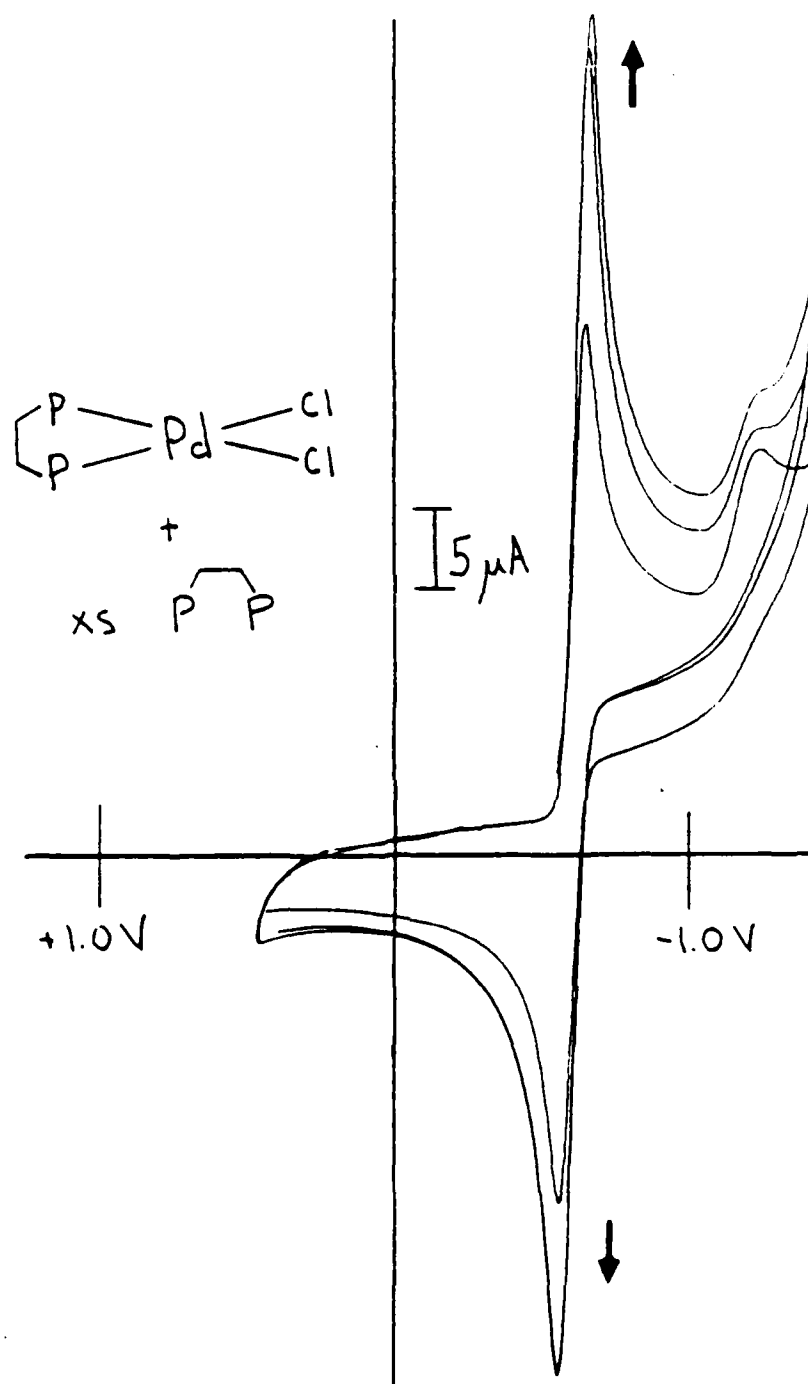Figure 9.   CV of <u>cis</u>-Pd(diphos)Cl$_2$ in TBAP/CH$_2$Cl$_2$

Figure 10.   Sequential   voltammograms of <u>cis</u>-Pd(diphos)Cl$_2$
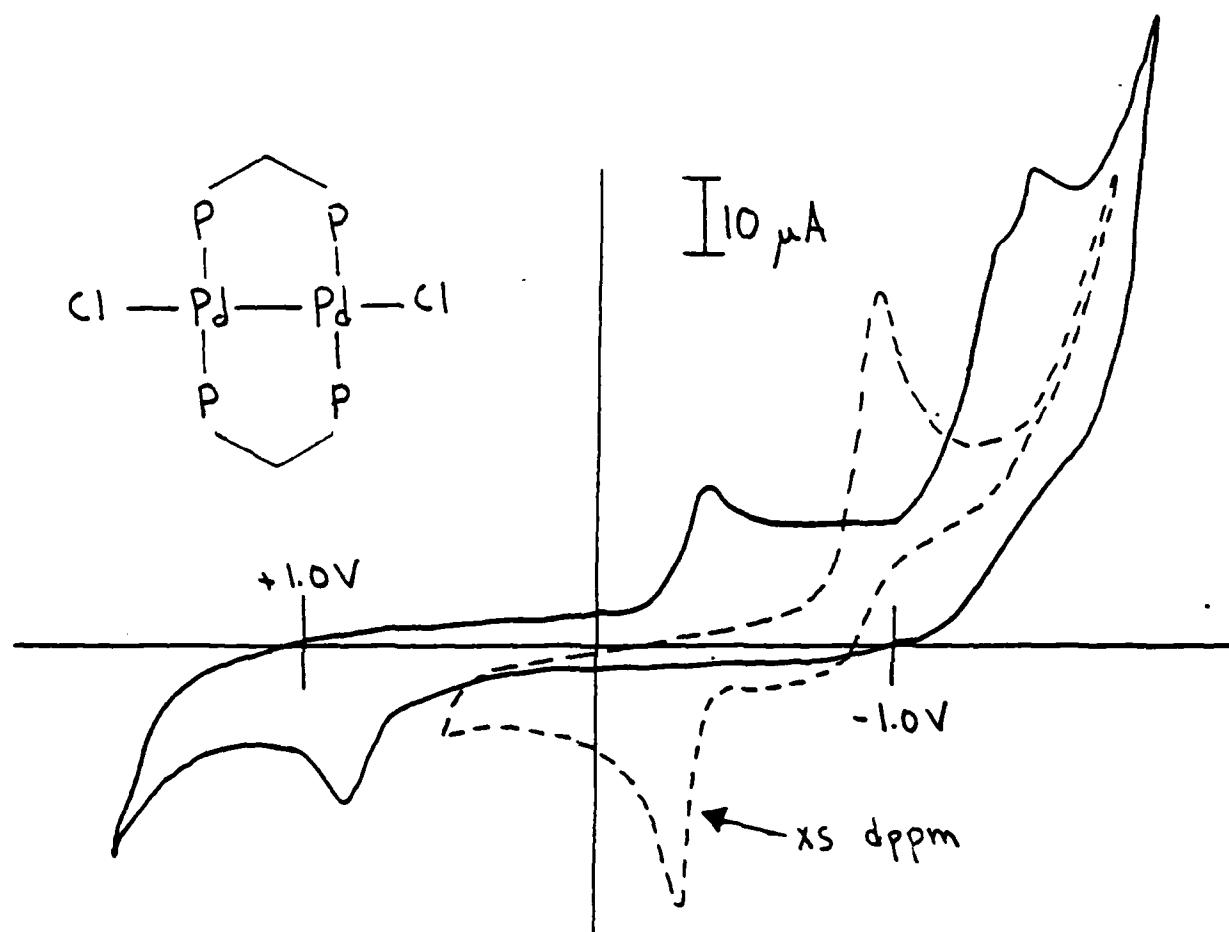after addition of excess diphos

Figure 11. CV of $Pd_2(\mu\text{-dppm})_2Cl_2$ in $TBAP/CH_2Cl_2$
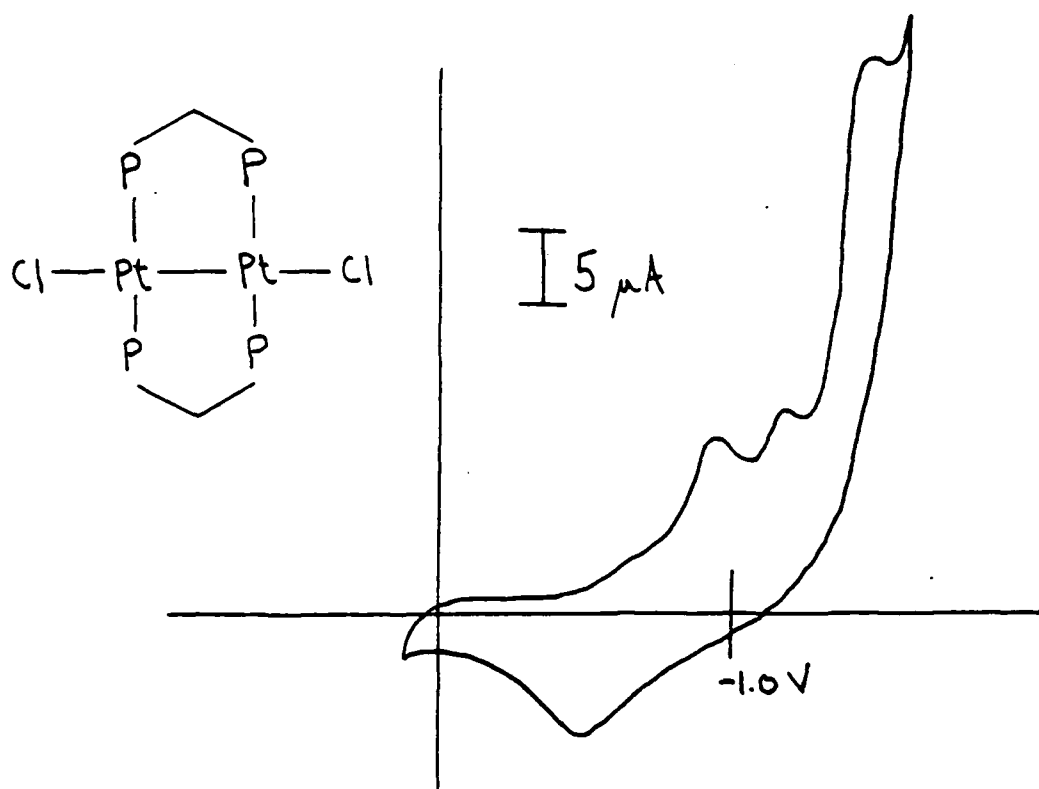
Figure 12. CV of $Pt_2(\mu\text{-dppm})_2Cl_2$ in $TBAP/CH_2Cl_2$

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